# Superior performance of multi-wall carbon nanotubes as support of Pt-based catalysts for the preferential CO oxidation: Effect of ceria addition

E.O. Jardim, M. Gonçalves, S. Rico-Francés, A. Sepúlveda-Escribano, J. Silvestre-Albero*

*Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica-Instituto Universitario de Materiales, Apartado 99, E-03080 Alicante, Spain*

## ARTICLE INFO

## ABSTRACT

Preferential oxidation of CO in excess hydrogen (PROX) was studied over Pt catalysts supported on multi-wall carbon nanotubes in the temperature range between room temperature and the temperature of the water–gas shift unit (∼473 K). Experimental results show that the Pt/CNT catalyst exhibit a superior performance in terms of catalytic activity and selectivity towards $CO_2$ formation compared to a Pt/AC catalyst prepared under similar conditions. Apparently, preferential CO oxidation in excess hydrogen over Pt nanoparticles supported on carbon materials is a *particle size* dependent reaction, i.e. larger particles exhibit higher activity and selectivity. In any case, the incorporation of oxygen functionalities to the carbon support becomes detrimental for the CO oxidation reaction independently of the carbon support used. Finally, $CeO_2$ addition to the Pt/CNT catalyst further improves both catalytic activity and selectivity at low temperatures (CO conversion rate of 46% at 313 K), the catalytic performance being superior to that exhibited by a traditional PROX catalyst such as $Pt/CeO_2$.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

Operational conditions in polymer electrolyte membrane fuel-cell technology (PEMFC) require the presence of "pure" hydrogen fuels, i.e. hydrogen streams without any significant pollutant. Nowadays, hydrogen is produced through the steam reforming of hydrocarbons or alcohols, followed by the water–gas shift reaction (WGS), with the subsequent formation of trace amount of carbon monoxide (0.5–1 vol.%) [1–3]. Taking into account that CO is a poison for the Pt-based anodes used in fuel cell technology at the operation temperature (∼353 K), CO must be selectively removed without modifying the hydrogen stream obtained after the WGS reaction. Among the different methods investigated, low temperature preferential CO oxidation in hydrogen-rich streams (PROX) is presently considered as the most promising and economic approach to decrease the CO concentration in WGS streams to the few ppm levels necessary for the efficient operation of fuel cells.

Reported catalysts for this reaction are based on noble metal nanoparticles (Pd, Pt, Rh and Ru) supported on oxide supports, mainly alumina [4–6]. In general, a suitable catalyst for the PROX reaction must adsorb and oxidize CO to $CO_2$ avoiding the competing adsorption and oxidation of $H_2$ to $H_2O$. Particle size and shape, oxidation state of the metal and the nature of the support have

been suggested as crucial factors defining both the catalytic activity and selectivity on this reaction. Among the different oxide supports analyzed, $CeO_2$ has been proposed as an excellent promoter for the CO oxidation reaction at low temperature due to its ability to supply active oxygen under oxygen lean environments [7–9]. Concerning non-oxide supports, Snytnikov et al. [10] reported a moderate activity and selectivity at low temperature for noble metal nanoparticles (Pd, Pt and Ru) supported on a special carbonaceous material. Further analysis using activated carbon as a support showed that the catalytic activity and selectivity could be slightly modified using two approaches, either by the incorporation of a second metal (e.g. PtSn/carbon) or by the addition of a partially reducible oxide (e.g. $Pt/CeO_2$/carbon) [11–13]. In any case, the reported results when using carbon as a support are still far away from the observed behaviour for the well-established $Pt/CeO_2$ catalyst, due to the absence of an additional oxygen supply at the metal–support interface. Recent studies by Tanaka et al. [14] have anticipated a promoting effect of carbon nanotubes when used as a support of Pt catalysts for the CO oxidation reaction. Although the carbon nanotubes used had low purity, catalytic measurements showed a large improvement in the CO conversion rate for high metal loadings (15 wt.% Pt).

Taking into account these premises, this manuscript compares the catalytic behaviour of Pt nanoparticles supported on high purity carbon nanotubes (CNT), with that of similar Pt nanoparticles supported on a conventional high surface area activated carbon. The effect of the Pt particle size, the surface chemistry of the carbon support and the effect of $CeO_2$ addition in both systems

* Corresponding author. Tel.: +34 96590 9350; fax: +34 96590 3454.
*E-mail address:* joaquin.silvestre@ua.es (J. Silvestre-Albero).

will be discussed for the preferential CO oxidation reaction under hydrogen-rich conditions. These catalysts will be evaluated in the temperature range from room temperature to the normal operation temperature of the low temperature WGS unit ($\sim$473 K), with special interest in obtaining catalysts with a high catalytic activity and selectivity towards $CO_2$ formation ($H_2$ oxidation to $H_2O$ must be avoided) at the normal operational temperature of PEMFC ($\sim$353 K) in on-board fuel processors.

## 2. Experimental

### 2.1. Preparation of the Pt catalysts

High purity multi-wall carbon nanotubes (i.d. 2–6 nm) were supplied by Bayer Materials Science (BAYTUBES C150 HP). As-received carbon nanotubes were submitted to an oxidation treatment with concentrated $HNO_3$ for 24 h at 403 K. After the oxidation treatment, carbon nanotubes were washed with distilled water until pH $\sim$7 and dried at 333 K overnight (CNTox). Pt/CNT and Pt/CNTox catalysts were prepared by wet impregnation using a basic (ammonium hydroxide) aqueous solution (pH 9) containing the appropriate concentration of Pt precursor ($Pt(NH_3)_4[NO_3]_2$) to achieve a Pt loading of 1 wt.%. For the sake of comparison, two conventional Pt/AC and Pt/ACox catalysts were prepared by wet impregnation of a commercial activated carbon (RGC-30) from Westvaco Corp., using the same experimental conditions both for the oxidation of the support and for the preparation of the catalysts. Activated carbon RGC-30 is a commercial sample characterized by a well-developed porous structure together with a very low ash content, i.e. absence of concomitant inorganic species, which could alter the catalytic process. After preparation, all catalysts were submitted to a thermal decomposition treatment at 673 K under a He flow (50 ml/min) for 1 h.

Two different $CeO_2$-promoted catalysts were prepared by wet impregnation of the as-received CNT and AC supports using an aqueous solution of $Ce(NO_3)_3 \cdot H_2O$. The final ceria loading was 20 wt.% in both cases. After the impregnation, both solids were submitted to a calcination treatment at 673 K under a He flow for 2 h. In a subsequent step, $Pt/CeO_2/CNT$ and $Pt/CeO_2/AC$ samples were prepared by wet-impregnation using an aqueous solution of $Pt(NH_3)_4(NO_3)_2$ with the appropriate concentration to achieve a 1 wt.% Pt loading. After Pt incorporation, both catalysts were submitted to a thermal treatment at 673 K, as described above, for 1 h.

### 2.2. Catalyst characterization

The textural properties of the different supports have been characterized using nitrogen adsorption measurements at 77 K. Gas adsorption experiments were performed in a home-made fully automated volumetric equipment. Prior to the adsorption experiment, samples were degassed under vacuum ($10^{-4}$ Pa) at 523 K for 4 h. The "apparent" surface area was estimated after application of the BET equation.

The chemical characterization of the as-received and acid modified carbon supports was performed using temperature-programmed decomposition measurements (TPD). TPD experiments were performed in a U-shape quartz reactor using a He flow (50 ml/min) up to 1273 K (heating rate 10 K/min). The amount of CO and $CO_2$ evolved was monitored by on-line mass spectrometry.

TEM micrographs were obtained on a JEOL model JEM-2010 electron microscope working at 200 kV, equipped with an INCA Energy TEM 100 analytical system and a SIS Megaview II camera. Samples for analysis were suspended in ethanol and placed on copper grids with a holey-carbon film support.
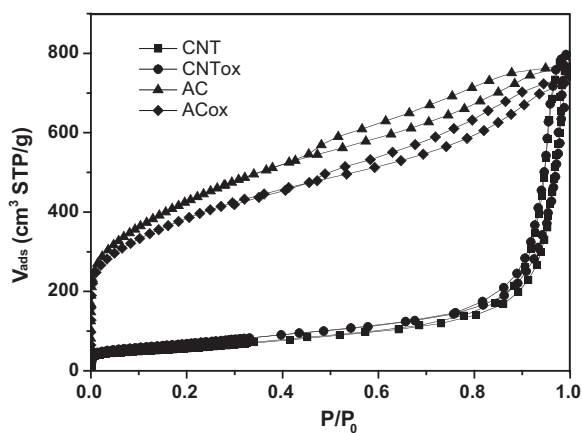


**Fig. 1.** Nitrogen adsorption/desorption isotherms for the CNT and AC materials before and after the oxidation treatment with $HNO_3$.

### 2.3. Catalytic behaviour

For the determination of the catalytic behaviour, the catalysts (100 mg) were placed in a U-shape quartz reactor. Before any catalytic measurement, the catalysts were in situ reduced under a hydrogen flow (50 ml/min) at 523 K for 1 h (heating rate, 5 K/min). The selective oxidation of CO in the presence of hydrogen (PROX) was studied in the temperature range 303–473 K and atmospheric pressure. The reaction mixture was 20% $H_2$, 2% CO, 2% $O_2$ and He as a balance (total flow: 50 ml/min and GHSV: 17,000 $h^{-1}$). Reaction products were analyzed by on-line gas chromatography (TCD), using a Plot/Q and a Molesieve capillary columns to separate the reactants and the products. The CO and $O_2$ conversion, as well as the selectivity towards $CO_2$, were calculated using the following equations:

$$X_{CO}(\%) = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100$$

$$X_{O_2}(\%) = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} \times 100$$

$$S_{CO_2}(\%) = \frac{0.5x[CO_2]_{out}}{[O_2]_{in} - [O_2]_{out}} \times 100$$

## 3. Results and discussion

### 3.1. Characterization of the selected carbon supports

Fig. 1 shows the nitrogen adsorption/desorption isotherms at 77 K for the multi-wall carbon nanotubes and the commercial activated carbon RGC-30, both as-received and after an oxidation treatment with $HNO_3$. The adsorption behaviour of the selected carbon materials differs considerable. Multi-wall carbon nanotubes exhibit a type II isotherm, according to the IUPAC classification, characteristic of nonporous carbon materials. Above a relative pressure of 0.8–0.9 a sudden increase in the amount adsorbed can be observed together with a well-defined hysteresis loop, traditionally attributed to the presence of mesoporosity. The "apparent" surface area estimated after application of the BET equation is 200 $m^2$/g. On the contrary, activated carbon RGC-30 exhibits a combination of type I and type IV isotherms, characteristic of a carbon material combining both a well-developed micro and mesoporosity. The "apparent" surface area estimated for the commercial activated carbon RGC-30 achieves a value of 1520 $m^2$/g. In both cases, a subsequent oxidation treatment with nitric acid produces only slight

**Table 1**
Textural properties of the different carbon samples obtained from the nitrogen adsorption measurements at 77 K.

| Sample | $S_{BET}$ (m²/g) | $V_o$ (cm³/g) | $V_{meso}$ (cm³/g) | $V_t$ (cm³/g) |
|--------|-----------------|---------------|--------------------|---------------|
| CNT    | 200             | 0.08          | 0.47               | 0.55          |
| CNTox  | 245             | 0.09          | 0.47               | 0.56          |
| AC     | 1520            | 0.52          | 0.69               | 1.14          |
| ACox   | 1365            | 0.48          | 0.60               | 1.08          |

differences in the porous structure. The incorporation of oxygen functionalities in the activated carbon RGC-30 produces a slight decrease in the amount of nitrogen adsorbed. This observation can be attributed to the partial collapse of the narrow microporous structure after the oxidation treatment, although a limited accessibility of the nitrogen molecule to the narrow micropores at 77 K, due to the oxygen surface groups on the pore mouth, cannot be ruled out [15,16]. The oxidation treatment with nitric acid of carbon nanotubes has been proposed in the literature as a proper way to open carbon nanotube ends, thus making accessible their internal tube space to gas molecules. However, nitrogen adsorption isotherms reported in Fig. 1 show that the oxidation treatment has no effect on the adsorption properties of the multi-wall carbon nanotubes supplied by Bayer Materials Science. Although TEM images (not shown) denote some degradation of the nanotube ends after the oxidation treatment, the presence of several closing shells in the interior of the tubes avoids their complete opening. Consequently, the incorporation of metal nanoparticles in the interior of the nanotubes in the subsequent preparation of catalysts will not be expected. Table 1 shows a compilation of the main textural properties for these carbon samples.

Besides changes in the porous structure, the oxidation treatment using nitric acid is a very effective method for the modification of the surface chemistry in carbon materials [16]. In order to analyze the surface chemistry of the modified samples, temperature programmed decomposition experiments were performed in the temperature range 303–1300 K under inert atmosphere (He). Fig. 2 shows the (a) $CO_2$ and (b) CO desorption profiles for all samples. The $CO_2$ desorption profile corresponds to the decomposition of the less-stable more acidic oxygen surface groups (carboxylic acid, lactone, etc.), whereas the CO desorption profile corresponds to the decomposition of the more stable basic oxygen functionalities (quinone, phenol, carbonyl, etc.) [17]. As it can be observed, the as-received CNT exhibits a poor surface chemistry with flat desorption profiles for both $CO_2$ and CO. On the contrary, the as-received activated carbon exhibits a certain amount of acidic groups decomposing in the temperature range from 400 K up to 1200 K together with some basic groups decomposing above 800–900 K. The oxidation of the CNT produces a slight increase in the amount of oxygen surface groups decomposing both as $CO_2$ and CO, this effect being more drastic on the commercial activated carbon with a larger surface area. In the latter sample, the oxidation treatment produces a drastic increase in the amount of oxygen surface groups decomposing both as $CO_2$ and CO. A quantitative analysis using the calibrated mass spectra signals provides a total amount desorbed of 0.54 mmol $CO_2$/g and 1.03 mmol CO/g for activated carbon RGC-30 after the oxidation treatment (see insets in Fig. 2 for quantitative data).

In summary, the physico-chemical characterization of the carbon materials selected as a support shows that multi-wall carbon nanotubes exhibits a very low surface area, mainly in the mesoporous range, together with a poor surface chemistry, both parameters being only slightly modified after an oxidation treatment with nitric acid. On the contrary, the activated carbon RGC-30 exhibits a well-developed micro- and mesoporous structure together with a rich surface chemistry, i.e. presence of oxygen
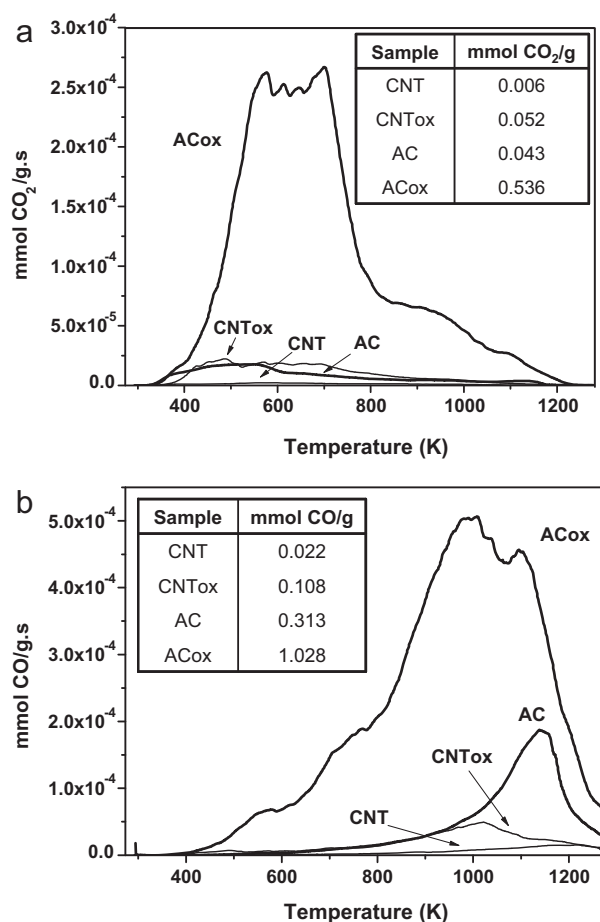


**Fig. 2.** Temperature programmed-decomposition (TPD) profiles for (a) $CO_2$ and (b) CO in the temperature range 303–1300 K for the as-received and oxidized CNT and AC.

functionalities, which is highly increased after the oxidation treatment.

### 3.2. Catalytic behaviour

#### 3.2.1. Effect of the carbon support

The as-received and modified carbon materials (CNT, CNTox, AC and ACox) have been used as support of Pt nanoparticles. Incorporation of 1 wt.% Pt on the surface of these supports has nearly no effect on the textural properties of the final catalyst, i.e. there is only a slight decrease in the BET surface area after Pt incorporation, thus reflecting the absence of blocking effect on the microporous structure of the carbon supports.

The catalytic performance of these samples has been tested in the preferential oxidation of CO in hydrogen rich conditions in the temperature range between 303 K and the normal operation temperature of the low-temperature WGS units (~473 K). As it can be observed in Fig. 3, the CO conversion rate is very poor at low temperatures (below 400 K) for all catalysts independently of the carbon support used (CO conversion below 20%). The poor catalytic activity of the monometallic Pt catalysts at low temperature must be attributed to the presence of strongly adsorbed CO species, which suppress oxygen adsorption and, consequently, the oxidation reaction [12]. A subsequent increase in the reaction temperature produces a moderate increase in the catalytic activity due to the partial desorption of CO from the noble metal surface and the decrease in the CO coverage, the light-off temperature being highly sensitive to the catalyst support used. Only Pt nanoparticles
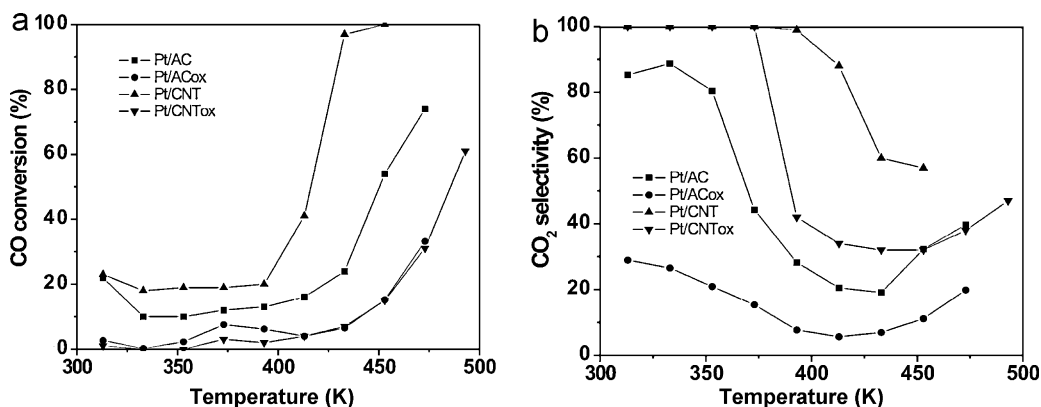
**Fig. 3.** (a) Catalytic activity and (b) selectivity for the different 1 wt.% Pt/CNT and 1 wt.% Pt/AC catalysts in the PROX reaction using both the as-received and the oxidized supports (feed composition: 20% $H_2$, 2% CO, 2% $O_2$ ($\lambda$ = 2) and He as a balance).

supported on the multi-wall carbon nanotubes (Pt/CNT catalyst) exhibit a drastic increase in the catalytic activity above 400 K, achieving 100% conversion at 433 K. On the contrary, the Pt/AC catalyst exhibits only 20% conversion at the same reaction temperature. The catalytic activity for Pt/AC is slightly lower than that reported by Manasilp and co-workers for $Pt/Al_2O_3$ catalysts under similar reactions conditions (~40% CO conversion rate at 433 K), whereas the Pt/CNT catalyst highly exceeds these values [5]. A closer look to the catalytic behaviour of the Pt nanoparticles supported on the as-received carbon supports (un-oxidized materials) evidence that the higher activity of the Pt/CNT catalyst compared to its Pt/AC counterpart remains over the whole temperature range. Previous studies described in the literature have shown a similar promoting effect of CNT compared to graphite and conventional activated carbons when used as a support of Pt catalysts [14,18]. Tanaka and co-workers attributed the higher activity of the Pt/CNT catalyst to the different dynamic of the reactants and products on the close nanotube surface (quasi-one dimensional motion) compared to the open graphite surface. A subsequent oxidation treatment with $HNO_3$, i.e. the incorporation of oxygen functionalities to the carbon supports (Pt/CNTox and Pt/ACox), gives rise to a decrease in the catalytic activity down to a CO conversion rate very similar for both catalysts.

Concerning the selectivity towards $CO_2$, Pt/CNT and Pt/CNTox catalysts exhibit complete conversion to $CO_2$ with no water formation in the low temperature range. Higher reaction temperatures favour $H_2$ adsorption and oxidation to $H_2O$, with the subsequent loss of selectivity, this effect being more drastic for the oxidized support. On the contrary, Pt nanoparticles supported on the conventional activated carbon RGC-30 exhibit a slightly lower selectivity (~89%) at low temperature, which also decreases with an increase in the reaction temperature. Pt/ACox catalyst exhibits a poor selectivity (~29%) over the whole temperature range analyzed. In any case, the selectivity to $CO_2$ in all catalysts decreases with an increase in the reaction temperature down to minimum at around 425–450 K, the selectivity increasing thereafter. This increase in the selectivity towards $CO_2$ formation at high temperatures must be attributed either to some carbon burn-off with oxygen or, more probably, to the evolution of $CO_2$ due to the decomposition of the more acidic oxygen functionalities coming from the carbon support. Consequently, the Pt/CNT catalyst exhibits very promising results in terms of CO conversion rate, selectivity towards $CO_2$ formation, and stability towards deactivation and $H_2$ oxidation to $H_2O$ (Pt/CNT catalyst is able to keep a high selectivity even at high temperatures due to the inhibition of the $H_2$ oxidation reaction).

In summary, the catalytic tests in the preferential CO oxidation in the presence of hydrogen show important differences when comparing Pt nanoparticles supported on multi-wall carbon nanotubes and on a conventional activated carbon. Multi-wall carbon nanotubes as a support give rise to a higher catalytic activity (CO conversion rate) and selectivity to $CO_2$ as compared to the Pt catalyst prepared using the activated carbon as a support. In both cases, the incorporation of oxygen functionalities becomes detrimental for the CO oxidation reaction.

At this point it is noteworthy to mention that the specific surface area of the activated carbon RGC-30 is around eight times larger than the available surface area on the carbon nanotubes. Consequently, one would expect a larger platinum dispersion on the AC support compared to the CNT and, consequently, a higher catalytic activity per gram of sample on the former catalyst. Concerning the oxidized supports, the presence of oxygen functionalities on the carbon surface together with the basic conditions used during the preparation of the catalysts would favour the interaction between the $-O^-$ groups on the carbon surface and the cationic platinum precursor $[Pt(NH_3)_4]^{2+}$. Thus, one would expect a larger platinum dispersion in the oxidized supports as compared to the as-received samples, and consequently, a larger activity in these samples. Taking into account these assumptions and the experimental results obtained, one can provide some insights about the critical role of the Pt particle size, i.e. platinum dispersion, in the catalytic activity and selectivity for the PROX reaction when using carbon as a support. Apparently, samples with a small Pt dispersion, i.e. large particle size, exhibit a higher catalytic activity and selectivity (e.g. Pt/CNT).

### 3.2.2. Effect of the Pt particle size

In order to assess the effect of the Pt particle size in the catalytic behaviour of Pt/CNT, the as-prepared catalyst have been subjected first to a thermal decomposition treatment in He (50 ml/min) at raising temperatures: 573 K, 673 K and 773 K for 1 h, followed by a reduction treatment in hydrogen (50 ml/min) at 523 K for 1 h, before being tested in the preferential CO oxidation reaction. Fig. 4 shows the HR-TEM images of the Pt/CNT catalysts after the thermal treatment at 573 K and at 673 K. As it can be observed, the mean Pt particle size increases with the thermal treatment going from 2 nm after the low temperature treatment up to 4 nm for the catalyst treated at 673 K. These results clearly suggest that Pt nanoparticles supported on the surface of the multi-wall carbon nanotubes must exhibit a high mobility, i.e. there is a low metal–support interaction, and, consequently, are highly sensible to the temperature of the decomposition treatment applied.
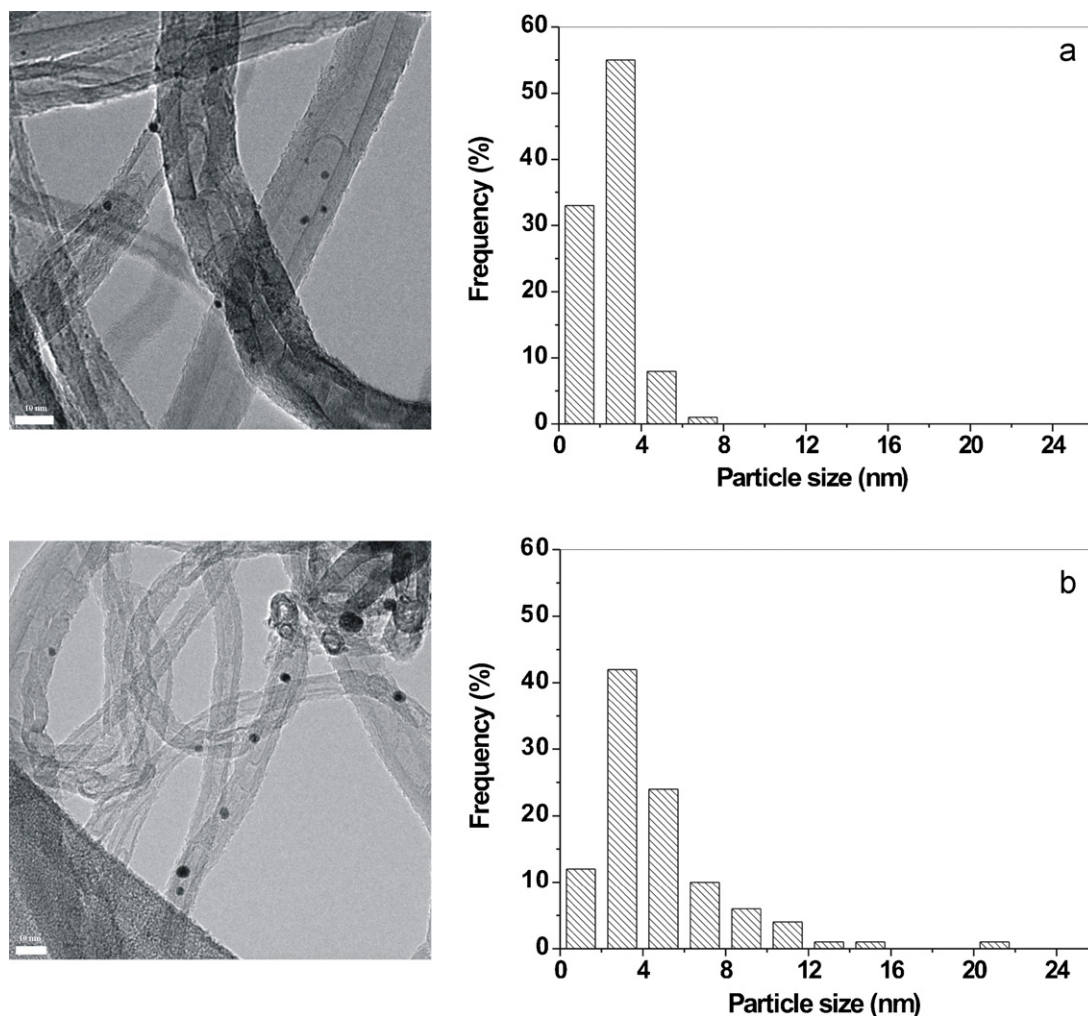
**Fig. 4.** TEM images of the Pt/CNT catalyst after a thermal decomposition treatment at (a) 573 K and (b) 673 K.

The catalytic behaviour of the thermally treated Pt/CNT catalysts in the preferential oxidation of CO (PROX) has been studied in the temperature range from 313 K up to 473 K. Fig. 5 shows the evolution of the (a) CO conversion rate and (b) selectivity to $CO_2$ for the different catalysts. As described before, Pt/CNT catalysts exhibit a poor conversion rate ($\sim$10–20% conversion) at low temperature (313–370 K), associated with a high selectivity (100%) towards $CO_2$ formation. Only the catalyst heat treated at high temperature (773 K) exhibits a slightly lower selectivity ($\sim$85%). Above 373 K,

important differences are observed for the different catalysts. In general, there is a sudden increase in the catalytic activity for all catalysts in a short temperature range ($\sim$20–40 K) up to complete CO conversion. However, the light-off temperature highly depends on the temperature of the thermal treatment applied, i.e. there is a large improvement in the catalytic activity with an increase in the temperature of the thermal treatment. In this sense, the Pt/CNT heat treated at 573 K achieves 100% CO conversion at a reaction temperature of 453 K, whereas the same catalyst heat treated at a higher
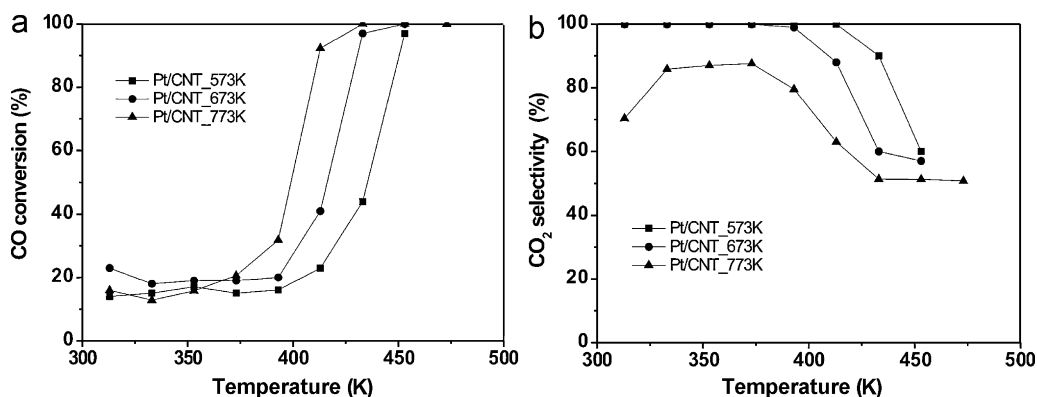


**Fig. 5.** Effect of the thermal treatment temperature on the (a) catalytic activity and (b) selectivity of 1 wt.% Pt/CNT catalysts in the PROX reaction at different reaction temperatures (feed composition: 20% $H_2$, 2% CO, 2% $O_2$ ($\lambda = 2$) and He as a balance).
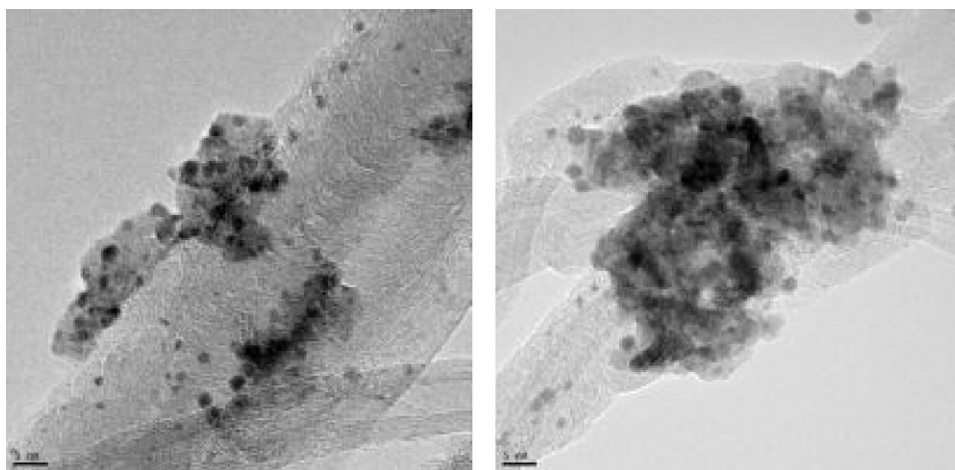
**Fig. 6.** TEM images of the calcined $Pt/CeO_2/CNT$ catalyst.

temperature (773 K) exhibits nearly complete conversion (∼93%) at a much lower temperature (413 K). The sudden increase in the CO conversion rate is accompanied by a decrease in the selectivity to $CO_2$ in all the catalysts, i.e. the $H_2$ oxidation reaction is favoured at high reaction temperatures. The final selectivity achieved is very similar for all catalysts around 50–60%. Taking into account the HR-TEM observations and the catalytic results described above, it is clear that the CO oxidation reaction in the presence of excess hydrogen is a *particle size* dependent reaction when using carbon as a support. Apparently, larger Pt nanoparticles favour CO oxidation at lower temperatures. Similar structure sensitivity effects on this reaction have been described in the literature for Pt model catalysts (e.g. single crystals) under UHV conditions [18,19]. These observations on Pt nanoparticles differ considerable from other transition metals (Co and Au), where an increased catalytic activity was observed for smaller nanoparticles [20,21].

It is well known that large noble metal nanoparticles exhibit well-defined (1 1 1) terraces, whereas small nanoparticles are highly defective and well-defined crystallographic planes cannot be identified [22]. According to these assumptions, catalytic results show that large Pt nanoparticles containing (1 1 1) terraces are more active for the CO oxidation reaction at low temperatures as compared to defective Pt nanoparticles. This observation can be attributed to the different strength of the Pt–CO bond depending on the Pt surface structure, i.e. weaker Pt–CO bond on larger nanoparticles [23]. Furthermore, selectivity results towards $CO_2$ formation (Fig. 5b) show that large Pt nanoparticles exhibit a slightly lower selectivity, i.e. the $H_2$ oxidation reaction is also promoted on large nanoparticles. These observations are in close agreement with electrochemical studies of the CO oxidation reaction on different single crystals, i.e. Pt(1 1 1) and Pt(1 0 0) [18,19]. According to these studies, oxidation of CO on Pt(1 1 1) occurs at a lower potential compared to Pt(1 0 0) surfaces. The easier electro-oxidation of CO on Pt(1 1 1) surfaces was attributed to the weaker adsorption of CO on (1 1 1) crystallographic surfaces. Furthermore, these studies showed that weakly adsorbed CO on (1 1 1) surfaces would block hydrogen adsorption less effectively, thus explaining the higher activity of larger Pt nanoparticles for the parallel hydrogen oxidation reaction.

### 3.2.3. Effect of $CeO_2$ addition

The use of partially reducible oxides as support has been proposed as an excellent approach to enhance the performance of Pt nanoparticles in the selective oxidation of CO. The promoting effect of the reducible oxide has been explained as due to a modification of the reaction mechanism from a Langmuir–Hinshelwood mechanism, where CO and $O_2$ compete for the active site in the noble metal surface, to a non-competitive dual-site mechanism where $CeO_2$ promotes the CO oxidation reaction by increasing the oxygen supply at the metal–support interface, as proposed by Mars and van Krevelen [24].

TEM images in Fig. 6 show that $CeO_2$ deposited on the surface of the carbon nanotubes ($Pt/CeO_2/CNT$ catalyst) forms small agglomerates or patches in the exterior of the nanotube wall. Concerning the Pt nanoparticles, TEM images shows a heterogeneous distribution of these nanoparticles with preferential location on the surface of the $CeO_2$ patches and not on the bare carbon support.

Concerning the catalytic behaviour of the ceria-promoted catalysts, Fig. 7 compares the catalytic activity and selectivity obtained with the $Pt/CeO_2/CNT$ catalyst with that of the parent Pt/CNT catalyst. As it can be observed, $CeO_2$ addition produces a drastic increase in the catalytic performance at low temperatures with a CO conversion rate of 82% at 353 K vs. 19% in the un-promoted sample. Concerning the selectivity towards $CO_2$ formation, the $Pt/CeO_2/CNT$ catalyst exhibits an excellent behaviour with a selectivity value between 50% and 70% at low temperatures. On the contrary, the incorporation of 20 wt.% $CeO_2$ to the conventional Pt/AC catalyst has a detrimental effect in the CO conversion rate with a nil catalytic activity up to 373 K together with a low selectivity. A similar CO conversion rate (below 35%) has been described in the literature for $Pt/CeO_2/AC$ catalysts with a smaller ceria content [11]. Apparently, the promotion effect of $CeO_2$ highly depends on the nature of the carbon support used, i.e. $CeO_2$ improves the catalytic behaviour of Pt/CNT systems whereas it becomes detrimental when using activated carbons as support. In this sense, CO electro-oxidation experiments on Pt/CNT catalysts have shown a similar improvement in the catalytic activity after $CeO_2$ addition [25]. Yuan and co-workers attributed the improved behaviour to the additional supply of oxygen species ($OH_{ads}$) by $CeO_2$ adjacent to Pt sites, and to the lower activation energy of the reaction between $OH_{ads}$ on $CeO_2$ and reacting with $CO_{ads}$ on adjacent Pt sites compared to the electro-oxidation of CO with OH species, both adsorbed on Pt. However, additional features must also be taken into account in order to explain the different promoting effect of $CeO_2$, i.e. the different nature of the $Pt–CeO_2$ interface sites, depending on the carbon support used (either CNT or AC).

Concerning the $Pt/CeO_2/CNT$ catalyst, the excellent catalytic behaviour reported in Fig. 7 highly exceeds that of bulk $Pt/CeO_2$ catalyst in terms of CO conversion and selectivity towards $CO_2$ formation at the normal working temperatures of the fuel cells (below 363 K). $Pt/CeO_2$ catalyst has been widely studied in the literature in the last few years for the preferential CO oxidation reaction in
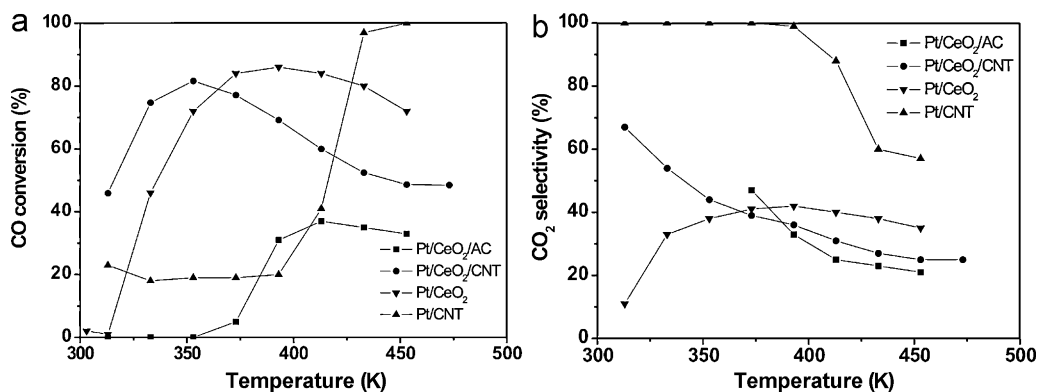
**Fig. 7.** Evolution of the (a) catalytic activity and (b) selectivity for a series of Pt catalysts as a function of the reaction temperature in the preferential oxidation of CO (PROX) (feed composition: 20% $H_2$, 2% CO, 2% $O_2$ ($\lambda = 2$) and He as a balance).

hydrogen reach streams [7,8,26]. Several authors have proposed this catalyst as a promising alternative for the selective CO oxidation reaction at the normal operational temperatures (~353 K) based on the ability of the reducible oxide to supply active oxygen at the metal–support interface. The higher activity of $CeO_2$-based carbon nanotubes as compared to bulk $CeO_2$ catalysts may result either from a higher ceria and platinum dispersion on the nanotube surface, which lead to an extensive Pt–Ce interaction, i.e. a larger number of metal–support interface sites, or to the larger oxygen supply in the $CeO_2$/CNT systems, i.e. lower activation energy, as compared to the bulk $CeO_2$. Most probably, hydroxyl groups on $CeO_2$ adjacent to Pt sites are more labile when supported on CNT, thus promoting the oxidation reaction at lower temperatures, i.e. larger ability of $CeO_2$ supported on CNT to incorporate oxygen from the gas phase and to transfer it to the active centers. However, further spectroscopic experiments are required to prove this hypothesis and to explain the poor behaviour of $CeO_2$ when supported on a high surface area activated carbon.

In summary, preferential CO oxidation measurements under hydrogen rich conditions show that Pt/$CeO_2$/CNT catalyst can be proposed as an excellent alternative to Pt/$CeO_2$ systems in terms of CO conversion rate and selectivity towards $CO_2$ formation for its application as a catalyst in the anode of PEMFC in on-board fuel processors at its normal operational temperature (~353 K).

## 4. Conclusions

Catalysts based on Pt nanoparticles supported on two different carbon materials, activated carbon (AC) and multi-wall carbon nanotubes, have been prepared and compared in the preferential CO oxidation reaction (PROX). The obtained results have shown that the best performance, in terms of activity and selectivity to $CO_2$, is obtained when CNT are used as support. Furthermore, it has been demonstrated that the presence of oxygen surface functionalities on the carbonaceous supports is detrimental for the catalytic behaviour. In addition, it has been found that an increase of the Pt particle size, obtained by increasing the thermal treatment temperature, yields more active catalysts, this confirming the *particle size* dependence of this reaction over platinum. Finally, the effect of $CeO_2$ as promoter has also been studied, and it has been found that its catalytic behaviour greatly depends on the carbon support used, in such a way that it improves the performance of Pt/CNT but poorer results are obtained when activated carbon is used as

support. In conclusion, Pt/$CeO_2$/CNT appears as a very promising system for the studied reaction.

## References

[1] D.S. Newsome, Catal. Rev. Sci. Eng. 21 (1980) 275–318.
[2] D.L. Trimm, Z.I. Onsan, Catal. Rev. Sci. Eng. 43 (2001) 31–84.
[3] A. Haryanto, S. Fernando, N. Murali, S. Adhikari, Energy Fuels 19 (5) (2005) 2098–2106.
[4] M. Echigo, N. Shinke, S. Takami, S. Higashiguchi, K. Hirai, T. Tabata, Catal. Today 84 (2003) 209–215.
[5] A. Manasilp, E. Gulari, Appl. Catal. B: Environ. 37 (2002) 17–25.
[6] S.H. Oh, R.M. Sinkevitch, J. Catal. 142 (1993) 254–262.
[7] F. Mariño, C. Descorme, D. Duprez, Appl. Catal. B: Environ. 54 (2004) 59–66.
[8] O. Pozdnyakova, D. Teschner, A. Wootsch, J. Kröhnert, B. Steinhauer, H. Sauer, L. Toth, F.C. Jentoft, A. Knop-Gericke, R. Schlögl, J. Catal. 237 (2006) 1–16.
[9] A. Wootsch, C. Descorme, D. Duprez, J. Catal. 225 (2004) 259–266.
[10] P.V. Snytnikov, V.A. Sobyanin, V.D. Belyaev, P.G. Tsyrulnikov, N.B. Shitova, D.A. Shlyapin, Appl. Catal. A: Gen. 239 (2003) 149–156.
[11] S. Özkara, A.E. Aksoylu, Appl. Catal. A: Gen. 251 (2003) 75–83.
[12] A.E. Aksoylu, M.M.A. Freitas, J.L. Figueiredo, Catal. Today 62 (2000) 337–346.
[13] M.M. Schubert, M.J. Kahlich, G. Feldmeyer, M. Hüttner, S. Hackenberg, H.A. Gasteiger, R.J. Behm, Phys. Chem. Chem. Phys. 3 (2001) 1123–1131.
[14] K. Tanaka, M. Shou, H. Zhang, Y. Yuan, T. Hagiwara, A. Fukuoka, J. Nakamura, D. Lu, Catal. Lett. 126 (2008) 89–95.
[15] F. Rodríguez-Reinoso, M. Molina-Sabio, M.A. Muñecas, J. Phys. Chem. 96 (1992) 2707–2713.
[16] A. Silvestre-Albero, J. Silvestre-Albero, A. Sepúlveda-Escribano, F. Rodríguez-Reinoso, Microporous Mesoporous Mater. 120 (2009) 62–68.
[17] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Orfao, Carbon 37 (1999) 1379–1389.
[18] L. Li, G. Wu, B.-Q. Xu, Carbon 44 (2006) 2973–2983.
[19] B. Beden, C. Lamy, N.R. de Tacconi, A.J. Arvia, Electrochim. Acta 35 (1990) 691–704.
[20] C.-Y. Lu, M.-Y. Wey, Fuel 86 (2007) 1153–1161.
[21] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, J. Catal. 115 (1989) 301–309.
[22] J. Silvestre-Albero, G. Rupprechter, H.-J. Freund, J. Catal. 240 (2006) 58–65.
[23] S. Mukerjee, J. Mcbreen, J. Electroanal. Chem. 448 (1998) 163–171.
[24] P. Mars, D.W. van Krevelen, Chem. Eng. Sci. 3 (1954) 41–59.
[25] H. Yuan, D. Guo, X. Li, L. Yuan, W. Zhu, L. Chen, X. Qiu, Fuel Cells 9 (2009) 121–127.
[26] D. Teschner, A. Wootsch, O. Pozdnyakova-Tellinger, J. Kröhnert, E.M. Vass, M. Hävecker, S. Zafeiratos, P. Schnörch, P.C. Jentoft, A. Knop-Gericke, R. Schlögl, J. Catal. 249 (2007) 318–327.